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THE MOVEMENT OF PARTICLES SUSPENDED IN FLUIDS AT REST
WHICH IS POSTULATED BY THE MOLECULAR-KINETIC THEORY OF HEAT

A. Einstein

Translation of "Über die von der molekularkinetischen
Theorie der Wärme geforderte Bewegung von in
ruhenden Flüssigkeiten suspendierten Teilchen;"
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THE MOVEMENT OF PARTICLES SUSPENDED IN FLUIDS AT REST
WHICH IS POSTULATED BY THE MOLECULAR-KINETIC THEORY OF HEAT

A. Einstein

ABSTRACT: Bodies suspended in fluids move so as to be visible under the microscope if they are large enough. The magnitude of this heat-induced movement, not yet experimentally observed, is calculated.

In this paper it is to be shown that in accordance with the molecular-kinetic theory of heat, bodies of microscopically visible size suspended in fluids must, in consequence of the molecular movement of heat, execute movements of such magnitude that those movements can easily be detected with a microscope. It is possible that the movements to be dealt with here are identical with the so-called "Brownian molecular movement"; the data available to me concerning the latter is so imprecise, however, that I was unable to form any judgment about it. /549*

If the movement to be treated here, together with the conformity to law expected of it actually can be observed, then classical thermodynamics even for microscopically distinguishable spaces are no longer to be regarded as precisely valid and an exact determination of true atomic size is then possible. If conversely, the prediction of that movement were to prove to be incorrect, a grave argument against the molecular-kinetic conception of heat would thereby be a reality.

§1. The Osmotic Pressure Ascribable to Suspended Particles

Let z moles of a nonelectrolyte be dissolved in partial volume V^* of a fluid of total volume V . If volume V^* is separated from the pure solvent by a wall permeable to the solvent but not to the dissolved substance, then that wall is acted upon by so-called osmotic pressure which, in the case of sufficiently large values for V^*/z , satisfies the following equation: /550

$$p V^* = R T z .$$

If, on the other hand, small suspended bodies are present in partial volume V^* of the fluid instead of the dissolved substance, bodies which likewise cannot pass through the wall permeable to the solvent, then, according to the classical theory of thermodynamics--at least when neglecting the gravitation of no interest to us here--one does not have to expect that a force is acting on the wall. That

*Numbers in the margin indicate pagination in the foreign text.

is because, according to the usual conception, the "free energy" of the system does not seem to depend upon the position of the wall and the suspended bodies but only on the total masses and qualities of the suspended substance, the fluid and the wall, as well as upon pressure and temperature. To be sure, energy and entropy of the boundary surfaces (capillary forces) would still be taken into consideration for computing the free energy. We can neglect them, however, as changes in size and nature of the contact surfaces may not occur in the case of the positional changes of the wall and of the suspended bodies to be considered.

From the standpoint of the molecular-kinetic theory of heat, however, one comes to another conception. According to that theory, a dissolved molecule differs from a suspended body solely due to size, and one does see why a number of suspended bodies should not be corresponded to by the same osmotic pressure as the identical number of dissolved molecules. One will have to assume that, in consequence of the molecular movement of the fluid, the suspended bodies execute a disordered movement in the fluid, albeit a very slow one. If they are prevented by the wall from leaving volume V^* , they will exert forces on the wall, just like dissolved molecules. Thus, if n suspended bodies are present in volume V^* , i.e., $n/V^* = \nu$ per unit of volume, and if neighboring ones among them are sufficiently far removed from one another, there will be a correlation to them on the part of an osmotic pressure p of the following magnitude:

$$p = \frac{RT}{V^*} \frac{n}{N} = \frac{RT}{N} \nu,$$

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In this, N denotes the number of actual molecules contained in a mole. In the next section it is to be shown that the molecular-kinetic theory of heat really leads to that enlarged conception of osmotic pressure.

§2. Osmotic Pressure from the Standpoint of the Molecular-Kinetic Theory of Heat¹

If $p_1, p_2 \dots p_l$ are state variables of a physical system which determine perfectly the momentary state of same (e.g. the coordinates and velocity components of all atoms in the system), and if the complete system of variation equations of those state variables of the form

$$\frac{\partial p_i}{\partial t} = \varphi_i(p_1 \dots p_l) \quad (i = 1, 2 \dots l)$$

¹It is presupposed in this section that the author's papers on the fundamentals of thermodynamics are familiar (cf. An. d Phys. 9, p. 417, 1902; 11, p. 170, 1903). An acquaintance with those papers, as well as with this section of the present paper, can be dispensed with for an appreciation of the results of the present paper.

is given, with $\sum \frac{\partial \varphi_v}{\partial p_v} = 0$, then the entropy of the system is given by means of the expression

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$$S = \frac{\bar{E}}{T} + 2\kappa \lg \int e^{-\frac{E}{2\kappa T}} dp_1 \dots dp_i.$$

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In this, T denotes absolute temperature, \bar{E} the energy of the system, E energy as a function of p_v . The integral is to be extended over all value combinations of p_v compatible with the postulates of the problem. κ is connected with the aforementioned constant N through the relation $2\kappa N = R$. For free energy F , therefore, we obtain

$$F = -\frac{R}{N} T \lg \int e^{-\frac{EN}{RT}} dp_1 \dots dp_i = -\frac{RT}{N} \lg B.$$

We can imagine a fluid enclosed in volume V ; in partial volume V^* of V let there be n dissolved molecules, or suspended bodies, which are held in volume V^* by a semipermeable wall; let the integration limits of integral B occurring in the expressions for S and F be influenced thereby. Let the total volume of the dissolved molecules, or suspended bodies, be small as opposed to V^* . In line with the aforementioned theory, let this system be completely represented by state variables $p_1 \dots p_l$.

If, now, even the molecular picture were established down to all details, the evaluation of integral B would nevertheless present such difficulties that there could scarcely be any thought of an exact computation of F . Here, however, we only need to know how F depends upon the magnitude of volume V^* , in which all dissolved molecules, or suspended bodies (called "particles" for short below), are contained.

We call x_1, y_1, z_1 the rectangular coordinates of the center of mass of the first particle, x_2, y_2, z_2 those of the second, etc., x_n, y_n, z_n those of the last particle, and give for the centers of mass of the particles the infinitely small parallelepiped-shaped domains $dx_1 dy_1 dz_1, dx_2 dy_2 dz_2 \dots dx_n dy_n dz_n$, all of which let be situated in V^* . Let there be sought the value of the integral occurring in the expression for F , with the restriction that the particle centers of mass lie in the domain just assigned to them. That integral, can in any case, be brought to the form

$$dB = dx_1 dy_1 \dots dz_n J$$

in which J is independent of $dx_1 dy_1$ etc., as well as of V^* , i.e., of the position of the semipermeable wall. J is, however, also independent of the special choice of positions of the center-of mass domains and of the value for V^* , as is to be

shown immediately. If, namely, there be given a second system of infinitely small domains for the particle centers of mass and denoted by $dx'_1 dy'_1 dz'_1$, $dx'_2 dy'_2 dz'_2 \dots dx'_n dy'_n dz'_n$, which domains may differ from those originally given only due to their position but not their magnitude, and all of which are likewise contained in V^* , then, analogously.

$$dB' = dx'_1 dy'_1 \dots dz'_n J',$$

applies, in which

$$dx_1 dy_1 \dots dz_n = dx'_1 dy'_1 \dots dz'_n.$$

Thus:

$$\frac{dB}{dB'} = \frac{J}{J'}.$$

From the molecular theory of heat given in the papers cited, however, it cannot be easily concluded¹ that dB/B or dB'/B is equal to the probability that, at a point of time taken arbitrarily, the particle centers of mass are in the domains $(dx_1 \dots dz_n)$ or in the domains $(dx'_1 \dots dz'_n)$. If, then, the movements of the individual particles are (with sufficient approximation) independent of one another, the fluid homogeneous and no forces are acting upon the particles, then, given equal magnitude of the domains, the probabilities proper to the two domain systems must be equal to one another, with the result that

$$\frac{dB}{B} = \frac{dB'}{B'}.$$

applies. From this and from the last found equation, however, it follows that

$$J = J'.$$

It is thus shown that J depends upon neither V^* nor $x_1, y_1 \dots z_n$. Through integration one obtains

$$B = \int J dx_1 \dots dz_n = J V^{*n}$$

and, from that,

$$F = - \frac{RT}{N} \{ \lg J + n \lg V^* \}$$

and

$$P = - \frac{\partial F}{\partial V^*} = \frac{RT}{V^*} \frac{n}{N} = \frac{RT}{N} \nu.$$

It has been shown through this analysis that the existence of osmotic pressure is a consequence of the molecular-kinetic theory of heat, and that, in accordance with that theory, dissolved molecules and suspended bodies of an equal number behave perfectly alike with respect to osmotic pressure in the case of great dilution.

¹A. Einstein, Ann. d. Phys. 11, p. 170, 1903.

§3. Theory of Diffusion of Small Suspended Spheres

Let suspended particles be irregularly distributed in a fluid. We intend to investigate the dynamic state of equilibrium of those particles, on the premise that the individual particles are acted upon by a force K which depends upon place but not upon time. For the sake of simplicity, let it be assumed that the force everywhere has the direction of the X -axis.

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Let ν be the number of suspended particles per unit of volume; thus, in the case of thermodynamic equilibrium, ν is such a function of x that the variation of free energy vanishes for any virtual displacement δx of the suspended substance. Thus, one has

$$\delta F = \delta E - T \delta S = 0.$$

Let it be assumed that the fluid has the cross section 1 perpendicular to the X -axis and is bounded by planes $x = 0$ and $x = l$. One then has

$$\delta E = - \int_0^l K \nu \delta x dx$$

and

$$\delta S = \int_0^l R \nu \frac{\partial \delta x}{\partial x} dx = - \frac{R}{N} \int_0^l \frac{\partial \nu}{\partial x} \delta x dx.$$

Thus, the equilibrium condition sought is

$$-K\nu + \frac{RT}{N} \frac{\partial \nu}{\partial x} = 0 \quad (1)$$

or

$$K\nu - \frac{\partial p}{\partial x} = 0.$$

The last equation asserts that equilibrium is afforded to force K by osmotic pressure forces.

We employ equation (1) in order to determine the diffusion coefficient of the suspended substance. We can interpret the dynamic equilibrium state just considered as the superposition of two processes running inversely, to wit:

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1. a movement of the suspended substance under the effect of force K acting on each individual suspended particle,

2. a diffusion action which is to be understood as a consequence of disordered movements of particles due to the molecular movement of heat.

If the suspended particles are spherical (radius of sphere P) and the fluid has a coefficient of friction k , then force K imparts the individual particle [sic] with velocity¹.

$$\frac{K}{6\pi k P},$$

and

$$\frac{v K}{6\pi k P}$$

particles pass through the cross-sectional unit per unit of time.

If, furthermore, D denotes the diffusion coefficient of the suspended substance and μ the mass of a particle, then, due to diffusion,

$$-D \frac{\partial(\mu v)}{\partial x} \text{ grams}$$

or

$$-D \frac{\partial v}{\partial x}$$

particles pass through the cross-sectional unit per time unit. Since dynamic equilibrium is to prevail, there must be:

$$\frac{v K}{6\pi k P} - D \frac{\partial v}{\partial x} = 0. \quad (2)$$

From the two conditions (1) and (2) found for dynamic equilibrium, one can compute the diffusion coefficient. One obtains:

$$D = \frac{RT}{N} \frac{1}{6\pi k P}.$$

Thus, the diffusion coefficient of the suspended substance depends -- besides upon universal constants and absolute temperature -- only upon the coefficient of friction of the fluid and upon the size of the suspended particles. /556

¹ Cf., for example, B. G. Kirchhoff, Vorlesungen über Mechanik, 26. Vorlesung [Lectures on Mechanics, 26. Lecture #4].

§4. The Disordered Movement of Particles Suspended in a Fluid and Their Relation to Diffusion

We now pass over to investigating more precisely the disordered movements which, caused by the molecular movement of heat, give rise to the diffusion investigated in the last section.

It must manifestly be assumed that each individual particle executes a movement which is independent of the movement of all other particles; also, the movements of one and the same particle in various time intervals will have to be understood as actions independent of one another, so long as we do not imagine those time intervals as selected too small.

Let us now introduce into the study a time interval τ which is very small compared to observable time intervals but still so large that the movements executed by a particle in two successive time intervals τ are to be understood as occurrences independent of one another.

Now let n suspended particles be present in a fluid as a whole. In a time interval τ the X-coordinates of the individual particles will be enlarged by Δ , whereby Δ has a different (positive or negative) value for each particle. A certain frequency law will apply to Δ ; the number dn of the particles which experience in time interval τ a displacement lying between Δ and $\Delta + d\Delta$ will be expressible through an equation of the form

$$dn = n \varphi(\Delta) d\Delta$$

whereby

$$\int_{-\infty}^{+\infty} \varphi(\Delta) d\Delta = 1$$

and φ is different from zero only for very small values of Δ and fulfills the condition

$$\varphi(\Delta) = \varphi(-\Delta)$$

We will now investigate how the diffusion coefficient depends upon φ , again restricting ourselves to the case that the number v of particles per unit of volume depends only upon x and t .

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Let $v = f(x, t)$ be the number of particles per unit of volume; we compute the distribution of particles at time $t + \tau$ from their distribution at time t . From the definition of function $\varphi(\Delta)$, there is easily derived the number of particles which at time $t + \tau$ are situated between two planes -- with abscissas x and $x + dx$ -- perpendicular to the X-axis. One obtains

$$f(x, t + \tau) dx = dx \cdot \int_{\Delta=-\infty}^{\Delta=+\infty} f(x + \Delta) \varphi(\Delta) d\Delta.$$

Since τ is very small, however, we can now set

$$f(x, t + \tau) = f(x, t) + \tau \frac{\partial f}{\partial t}.$$

Furthermore, we expand $f(x + \Delta, t)$ by powers of Δ :

$$f(x + \Delta, t) = f(x, t) + \Delta \frac{\partial f(x, t)}{\partial x} + \frac{\Delta^2}{2!} \frac{\partial^2 f(x, t)}{\partial x^2} + \dots \text{to infinity}$$

We can undertake this expansion below the integral, inasmuch as only very small values of Δ contribute something to said integral. We obtain:

$$\begin{aligned} f + \frac{\partial f}{\partial t} \cdot \tau &= f \cdot \int_{-\infty}^{+\infty} \varphi(\Delta) d\Delta + \frac{\partial f}{\partial x} \int_{-\infty}^{+\infty} \Delta \varphi(\Delta) d\Delta \\ &+ \frac{\partial^2 f}{\partial x^2} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2} \varphi(\Delta) d\Delta \dots \end{aligned}$$

In the right member the second, fourth, etc. term vanishes on account of $\varphi(x) = \varphi(-x)$, whereas, of the first, third, fifth, etc. term, each successive one is very small as opposed to the preceding one. We obtain from this equation, taking into account that

$$\int_{-\infty}^{+\infty} \varphi(\Delta) d\Delta = 1,$$

and setting

$$\frac{1}{\tau} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2} \varphi(\Delta) d\Delta = D$$

and taking only the first and third term of the right member into account:

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}. \quad (1)$$

This is the familiar differential equation for diffusion, and one recognizes that D is the coefficient of diffusion.

Another important consideration can be joined to this development. We have assumed that the individual particles are all relative to the same coordinate system. That is not necessary, however, inasmuch as the movements of the individual particles are independent of one another. We now want to relate the movement of each particle to a coordinate system whose origin coincides with the position of the center of mass of the particle concerned

at time $t = 0$, with the difference that now $f(x,t)dx$ denotes the number of particles whose X-coordinates [sic] has grown from time $t = 0$ to time $t = t$ by a magnitude which lies between x and $x + dx$. In this case, too, function f thus changes in accordance with equation (1). Furthermore, for $x \geq 0$ and $t = 0$, there must manifestly be

$$f(x,0) = 0 \quad \text{and} \quad \int_{-\infty}^{+\infty} f(x,t) dx = n$$

The problem, which coincides with the problem of diffusion from one point (neglecting the interaction of the diffusing particles), is now determined to perfection mathematically; its solution is:

$$f(x,t) = \frac{n}{\sqrt{4\pi D}} e^{-\frac{x^2}{4Dt}} \frac{1}{\sqrt{t}}$$

The frequency distribution of the positional changes occurring in an arbitrary time t is thus the same as that of the accidental errors, which was to be suspected. Of significance, however, is how the constant in the exponent is connected with the diffusion coefficient. Now, with the help of that equation, we compute displacement λ_x in the direction of the X-axis that a particle experiences on the average, or -- expressed more precisely -- the root of the arithmetic mean of the squares of the displacements in the direction of the X-axis; it is

$$\lambda_x = \sqrt{x^2} = \sqrt{2Dt}.$$

The mean displacement is, therefore, proportional to the square root of the time. One can easily show that the root of the mean value for the squares of the total displacements of the particles has value $\lambda_x \sqrt{3}$.

§5. Formula for the Mean Displacement of Suspended Particles. A New Method for Determining the True Size of the Atoms.

In Section 3 we found the following value for the diffusion coefficient D of a substance in the form of small spheres of radius P suspended in a fluid:

$$D = \frac{RT}{N} \frac{1}{6\pi\eta P}.$$

In Section 4, furthermore, we found the following for the mean value of the displacements of the particles in the direction of the X-axis in time t :

$$\lambda_x = \sqrt{2Dt}.$$

By eliminating D, we obtain

$$\lambda_x = \sqrt{t} \cdot \sqrt{\frac{RT}{N} \frac{1}{3\pi k P}}.$$

This equation reveals how λ_x must depend upon T, k and P.

We intend to compute how great λ_x is for a second if N is set as $6 \cdot 10^{23}$ in accordance with the results of the kinetic theory of gases; let water of 17°C be selected as the fluid ($k = 1.35 \cdot 10^{-2}$) and particle diameter be 0.001 mm. One obtains

$$\lambda_x = 8 \cdot 10^{-5} \text{ cm.} = 0.8 \text{ micron.}$$

Thus, the mean displacement in 1 minute would be appr. 6 microns.

Conversely, the relation found can be employed to determine N. One obtains

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$$N = \frac{t}{\lambda_x^2} \cdot \frac{RT}{3\pi k P}.$$

May a researcher soon succeed in settling the question raised here which is of importance to the theory of heat!

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